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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : **C03C 4/02, 3/087**	A1	(11) International Publication Number: **WO 95/16641** (43) Internati nal Publicati n Date: 22 June 1995 (22.06.95)

(21) International Application Number: PCT/GB94/02496

(22) International Filing Date: 14 November 1994 (14.11.94)

(30) Priority Data:
168,347 17 December 1993 (17.12.93) US

(71) Applicant (*for all designated States except GB*): FORD MOTOR COMPANY [US/US]; County of Wayne, Dearborn, MI 48126 (US).

(71) Applicant (*for GB only*): FORD MOTOR COMPANY LIMITED [GB/GB]; Eagle Way, Brentwood, Essex CM13 3BW (GB).

(72) Inventors: JONES, James, Victor; 5755 Snowden Drive, Toledo, OH 43623 (US). BOULOS, Edward, Nashed; 4395 Stonehenge Court, Troy, MI 48098 (US).

(74) Agent: MESSULAM, Alec, Moses; A. Messulam & Co., 24 Broadway, Leigh on Sea, Essex SS9 1BN (GB).

(81) Designated States: BB, CA, CN, HU, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: GLASS COMPOSITION

(57) Abstract

A neutral grey, heat absorbing soda-lime-silica glass having at 4 mm. control thickness a light transmittance using illuminant A of 10.0 % to 55.0 %, ultra violet transmittance less than 25.0 %, and infrared transmittance is less than about 50.0 % produced with colourants consisting of 0.90 to 1.90 percent by weight total iron oxide as Fe_2O_3, 0.002 to 0.025 percent Co, 0.0010 to 0.0060 percent Se, 0.10 to 1.0 percent MnO_2, and 0 to 1.0 percent TiO_2. The flat glass products having such a composition is particularly suitable for use as a privacy glass or sun roof product in trucks and automobiles.

GLASS COMPOSITION

This invention is directed to a heat absorbing, neutral grey coloured glass composition. More particularly, it comprises soda-lime-silica glass whose colouring components consist essentially of iron oxide, cobalt, selenium, manganese dioxide, and optionally titanium dioxide.

Glass having a neutral grey colour and properties such as low infra red transmittance and low total solar energy transmittance which reduce the heat gain in the interior of an enclosure is highly desired in the automotive field. The neutral grey colour is chosen for the sake of coordinating with a wide range of automotive paint colours. To be particularly useful in the automotive field, the glass composition should be one that is compatible with flat glass manufacturing methods. A glass composition having these properties would be highly desirable, particularly for automotive privacy and sun roof applications.

Some other heat absorbing grey glass compositions contain selenium as an essential colouring component. For example, U.S. Patent 4,873,206 to Jones discloses a grey glass composition which includes as the colourants only iron, cobalt, and selenium. Selenium is a relatively low melting component with a melting point of 217°C and a boiling point of 685°C which typically leads to a volatilisation of 85% or more of the selenium from the glass batch during glass melting and processing. Selenium is a very expensive material and hence its emission during glass melting is less than desirable. This high level of volatilisation takes place even though glass manufacturers typically use sodium or potassium nitrates in the glass composition in an attempt to retain more of the selenium in the glass product.

The present invention overcomes problems associated with selenium vaporisation by incorporating manganese oxide

into a grey glass composition along with the selenium. We have unexpectedly found that incorporating the manganese oxide into a selenium containing glass composition aids in selenium retention during melt processing.

In addition, contrary to the suggestion of Jones in the patent listed above, including manganese oxide in the present invention composition along with the iron oxide did not lead to increased solarisation. Solarisation is the result of reactions that occur in glass when exposed to UV radiation such as that in sunlight. One such reaction is the shift of Fe^{+3} towards Fe^{+2}. Solarisation causes the iron to move from the oxidised species to the reduced species which also causes an undesirable colour shift in the glass product. This problem of solarisation is also discussed by Milos B. Volf in <u>Chemical Approach to Glass</u>, Elsevier Science Publishing Co., Inc., 1984, p. 343. "Manganese as a decolouriser has the disadvantage of creating solarisation and of being sensitive to the furnace atmosphere."

Generally, grey coloured heat absorbing glasses relied, in the past, on the inclusion of nickel oxide as an active colouring agent. Nickel compounds, however, are known to react with other materials in soda-lime-silica glass and form nickel sulphide "stones" in the glass. These stones are usually small, thereby avoiding detection methods, but can produce an unacceptably high rate of breakage during tempering of the glass. U.S. Patent 5,023,210 to Krumwiede et al. discloses the use of chrome oxide in combination with iron oxide, cobalt oxide and selenium to achieve a dark grey glass without nickel. It does not include MnO_2.

The present invention is a soda-lime-silica glass composition that is heat absorbing with a neutral grey colour and improved selenium retention. The composition in its broadest embodiment comprises 68 to 75% SiO_2, 10 to 18% Na_2O, 5 to 15% CaO, 0 to 10% MgO, 0 to 5% Al_2O_3, and 0 to 5% K_2O, where CaO + MgO is 6 to 15% and Na_2O + K_2O is 10 to

20%, with traces of melting and refining aids, if any, and colourants consisting essentially of: 0.90 to 1.90 wt.% total iron oxide as Fe_2O_3; 0.002 to 0.025 wt.% cobalt as Co; 0.0010 to 0.0060 wt.% selenium as Se; 0.10 to 1.0 wt.% manganese oxide as MnO_2; and 0.0 to 1.0% titanium oxide as TiO_2.

Glass products made according to embodiments of the invention have the following spectral properties at 4mm thickness: 10.0 to 55.0% light transmittance using illuminant A (LTA), less than 25.0% ultra violet transmittance, and less than 50.0% infra red transmittance. Preferably, the composition has a dominant wavelength between about 470 and 590 nanometres. Generally, as the quantities of the colourants increase, the % transmittance will go down. Similarly, generally as the glass thickness increases for a given glass composition, the transmittance of the thicker glass will decrease.

We have unexpectedly discovered that introducing manganese oxide in the batch increases the retention of selenium in the glass product over and above that obtained by incorporating nitrates. While the major function of the manganese oxide is to increase the selenium retention, there is some absorption by manganese oxide in the same portion of the visible spectrum as the selenium component, hence incorporation of manganese oxide also further enhances the grey colour. Thus, less of the costly selenium is necessary to be present in the composition since the manganese oxide in effect also acts to provide the grey colour. Desirably, the glass composition of this invention has a grey colour which is obtained without the addition of nickel.

Flat soda-lime-silica glass, used in the automotive and architectural industries and conveniently made by the float glass process, is generally characterised by the following basic composition shown in Table I, the amounts of the components being based on a weight percentage of the total glass composition:

Table I

Oxide Component	Weight %
SiO_2	68 to 75
Al_2O_3	0 to 5
CaO	5 to 15
MgO	0 to 10
Na_2O	10 to 18
K_2O	0 to 5

The neutral grey glass composition of the present invention employs this basic soda-lime-silica glass composition wherein, additionally, CaO + MgO is 6 to 15% and Na_2O + K_2O is 10 to 20%. Preferably SO_3 is 0.10 to 0.30 wt. %, more preferably 0.14 to 0.25 wt. %. In addition, the neutral grey glass composition consists essentially of the following colouring components: iron oxide; cobalt oxide; selenium; manganese oxide; and optionally titanium dioxide as summarised above.

The total iron oxide as Fe_2O_3 is present in the invention composition in quantities of 0.9 to 1.90 weight %. All weight percents disclosed herein are based on the total weight of the invention glass composition. Typically, this ingredient is added into the batch ingredients in oxide form, e.g., Fe_2O_3. The iron oxide incorporated in the composition lowers both the ultra violet and the infra red transmittance of the glass products. More particularly, the iron oxide performs two functions in this glass system: (1) the oxidised form of iron oxide (Fe_2O_3) absorbs in the ultra violet portion of the spectrum providing low ultra violet transmittance, and (2) the reduced form of iron oxide (FeO) absorbs in the infra red portion of the spectrum and the resultant glass thus has a lowered infra red transmittance. Both absorbing functions of the iron oxide are especially

valuable when the glass product is used in automobiles. When heat is absorbed by the glass, the load on air conditioners is initially reduced and there is less total heat in the vehicle to cool.

Cobalt, which is typically added to the batch ingredients as an oxide thereof, is present as a colouring component in the invention glass composition in an amount of 0.002 to 0.025 wt. % as Co, the cobalt functioning to absorb light from about 580 to 680 nanometres in the visible portion of the spectrum. Selenium, which is typically added to the batch ingredients as a metal, is present as a colouring component in an amount of 0.0010 to 0.0060 wt.% Se, the selenium functioning to absorb light from about 430 to 540 nanometres of the visible spectrum. It is necessary to balance the amount of absorption from selenium with that of cobalt to achieve a neutral grey appearance.

Manganese oxide is present in the grey glass invention composition in an amount of 0.10 to 1.0 wt % based on MnO_2. Manganese oxide can be added to the batch glass components in a variety of forms, e.g., MnO_2, MnO_4, MnO, etc. In the glass composition, it is generally present in the Mn^{+2} and Mn^{+3} state, although it may additionally be present in other states such as Mn^{+4}. There are two functions that manganese oxide performs in the present invention composition: (1) one form of manganese in the glass absorbs in the same area as selenium so that it replaces a portion of the selenium, and (2) manganese oxide acts as an oxidiser and helps to retain a larger proportion of selenium from the batch. Typically, in compositions without manganese oxide, a large amount of selenium (about 85-90%) which is very costly volatilises from the batch even when using sodium or potassium nitrates as oxidisers. Therefore, our finding that manganese oxide is extremely beneficial in retaining a higher proportion in the final glass product of the selenium added into the batch (~300% increased selenium retention) was unexpected and is a critical point of this invention. As discussed above and in

more detail below, unexpectedly we have also found that contrary to prior teachings, including manganese oxide along with iron oxide in the glass composition did not cause any appreciable solarisation (discolouring) after exposure to ultra-violet light. We have discovered that employing manganese oxide along with iron oxide in amounts as specified in this invention composition, allows the solarisation phenomena to be minimised.

Titanium dioxide may optionally be used in the present invention neutral grey glass composition to enhance achievement of a particular range of dominant wavelength to the glass composition. Grey glasses of this invention are preferably those with an excitation purity of less than about 5.5%. It is important that the present invention glass product be a neutral grey, more specifically being a green grey; preferably the dominant wavelength with illuminant C is between 470 and 590 nanometres (nm), more preferably between 480 and 570nm, most preferably between 487.5 and 558nm, using the C.I.E. convention with a 2° observer. Titanium dioxide is very useful in shifting the dominant wavelength within the range of 470 to 590 nanometres. Titanium dioxide also absorbs in the ultra violet range of the spectral curve and helps to lower the ultra violet transmittance of glass in this invention.

We have found that glasses within the broadest scope of this invention have the following spectral properties when measured at a control thickness of 4.0 millimetres: light transmittance with illuminant A (LTA) between 10.0% and 55.0%, ultra violet transmittance of less than 25.0%, preferably less than about 10.0% when the glass has less than 35.0% LTA, and infra red transmittance is less than about 50.0%. As would be apparent to those skilled in the art in view of the present disclosure, the glass composition of this invention may also be made into glass at other thicknesses. Generally, although not meant to be so limited, the thickness for the glass product would be within

the range of 2.0 to 12.0 millimetres which is typical of glass produced by the float process.

Table II discloses the amounts of raw material batch ingredients which are preferably used to form embodiments of neutral grey glass compositions according to the present invention.

Table II

BATCH MATERIAL	RANGE MASS (LBS.)
Sand	1000
Soda Ash	290 to 320
Dolomite	215 to 260
Limestone	75 to 90
Salt Cake	6 to 24
Rouge (97% Fe_2O_3)	17 to 23
Titanium Dioxide	0 to 5
Sodium Nitrate	3 to 20
Manganese Dioxide	2 to 8
Carbocite (70% C)	0.1 to 1.5
Cobalt Oxide (Co_3O_4)	0.30 to 0.36
Selenium	0.20 to 0.70

As would be appreciated by those skilled in the art, processing aids are generally added to the glass batch during the melting and processing, e.g., to maintain the proper balance of redox conditions or as fining agents. For example, carbocite (anthracite coal) when added to the glass composition has the effect of reducing a portion of the Fe_2O_3 to FeO to achieve lower infra red transmittance. Sodium and/or potassium nitrate are used in glass batches of the invention to maintain oxidising conditions early in the

melting process which aids in selenium retention. Nitrates have been used by others to improve selenium retention. Careful balance must be maintained between the reducing conditions from the carbocite and the oxidising conditions from the nitrates and manganese dioxide used to improve selenium retention in the glass, because the oxidisers also act upon the iron oxide to shift the redox from FeO toward Fe_2O_3 while carbocite shifts the iron oxide equilibrium in the opposite direction. As disclosed above, we have discovered that employing manganese oxide along with iron oxide in the amounts specified for the invention composition, allows the solarisation phenomena to be minimised. The quantities of salt cake, carbocite and sodium nitrate preferably used in the batch ingredients to achieve the desired ratio between the two iron oxides in the final composition also helps to retard solarisation in the invention glass. More preferably, the lbs. of batch materials: salt cake; sodium nitrate; carbocite is 8-18; 5-15; 0.3-1.0, and most preferably are: 8-12; 5-10; 0.3-1.0, respectively per 1000lbs. of sand. These disclosed most preferred amounts of the three batch materials is associated with a final glass product preferably having 0.15-0.60 wt. % MnO_2 and 1.2-1.6 wt.% total iron as Fe_2O_3 in the final glass composition.

In order to show the unexpected effects of manganese dioxide on improving selenium retention in our glass composition, eight grey glass compositions were made as described below in Tables III and IV. Neutral grey glass compositions made according to embodiments of this invention were detailed as Examples 1-4. For comparison, similar glass compositions except without manganese dioxide were made as detailed as Examples 5-8. All of these glasses were made by the following procedure. The batches were weighed (typically 170 grams total) on a laboratory balance and mixed within a glass jar for 10 minutes each using a laboratory shaker. Each mixed batch was placed into a platinum-rhodium crucible which was about 2" tall with about

a 2.5" inside diameter and 4.5 ml. of water was mechanically mixed into the raw batch. Crucibles were placed into a natural gas/air furnace pre-heated to 2600°F with 3 to 5 other crucibles. Furnace temperature recovers to 2600°F in about 30 minutes. After two hours melting, each crucible was removed in turn, glass in the crucible was fritted by quenching in cold water, and the fragments were mixed in the crucible and all crucibles were returned to the furnace. Furnace temperature was brought back to 2600°F and the fritting procedure was repeated as in the step above once the operating temperature was attained, about 45 minutes. All glass samples were melted for another 3 hours and each sample was poured into a 2.5" inside diameter graphite mould to shape the glass samples for subsequent grinding and polishing. All samples were placed into an annealing furnace, brought up to 1050°F, held for 4 hours, then allowed to slowly cool to room temperature in about 16 hours. Samples were ground and polished and spectral properties were measured on each sample; spectral properties were calibrated to a control thickness of 4 mm. Samples were then chemically analysed via X-Ray fluorescence or other tests conducted as needed.

Table III

	Example 1	Example 2	Example 3	Example 4
Sand	100.00	100.00	100.00	100.00
Soda Ash	31.41	31.41	31.41	31.41
Limestone	7.25	7.25	7.25	7.25
Dolomite	25.83	25.83	25.83	25.83
Salt Cake	1.0956	1.0960	1.0969	1.0969
Sodium Nitrate	0.5215	0.5192	0.5233	0.5236
Rouge	1.8133	2.1103	1.9683	2.1061
Carbocite	0.0916	0.0914	0.0916	0.0907
Cobalt Oxide	0.0142	0.0313	0.0370	0.0392
Manganese Dioxide	0.5304	0.8107	1.3750	0.5315
Selenium	0.0209	0.0490	0.0430	0.0577
ppm Selenium in Glass	26	75	70	80
% Selenium Retained	17.1	21.0	22.3	19.0

Present invention compositions of Examples 1-4 show amounts of retained selenium of between 17.1 and 22.3%. In contrast, comparative Examples 5-8 below, not according to this invention (i.e., not including MnO_2) show amounts of retained selenium of only between 6.2 and 7.8%. These examples show an almost 300% increase in selenium retention when manganese dioxide is employed along with the selenium as in the present invention compositions.

Table IV

	Example 5	Example 6	Example 7	Example 8
Sand	100.00	100.00	100.00	100.00
Soda Ash	31.41	31.41	31.41	31.41
Limestone	7.25	7.25	7.25	7.25
Dolomite	25.83	25.83	25.83	25.83
Salt Cake	1.0961	1.0960	1.0960	1.0958
Sodium Nitrate	0.5187	0.5234	0.5220	0.5188
Rouge	2.1078	1.8144	2.1105	2.1051
Carbocite	0.0912	0.0913	0.0912	0.0917
Cobalt Oxide	0.0165	0.0144	0.0317	0.0389
Selenium	0.0286	0.0414	0.0963	0.1116
ppm Selenium in Glass	8	10	22	28
% Selenium Retained	7.8	6.5	6.2	6.2

Table V below lists the preferred ranges of resultant oxide constituents of our new glass composition. Following the table are the spectral properties of such preferred glass compositions according to the invention.

Table V

Oxide Component	Weight %
SiO_2	71 to 74
Al_2O_3	0.15 to 0.25
Fe_2O_3	1.20 to 1.60
CaO	8.40 to 8.70
MgO	3.5 to 4.00
Na_2O	13.00 to 13.80
K_2O	0 to 0.10
TiO_2	0.00 to 0.35
MnO_2	0.15 to 0.6
SO_3	0.14 to 0.25
Co (metal)	0.0160 to 0.0185
Se (metal)	0.0020 to 0.0040

Preferred Glass Property Ranges (4 mm. thick glass sheet)

Visible Transmission (Ill. A):	16-20 %
Ultraviolet Transmission:	5-10 %
Infrared Transmission:	10-18 %
Total Solar Transmission:	12-20 %
Dominant Wavelength:	470-590nm
Excitation Purity:	0.0-5.5%
FeO/Total Iron Oxide as Fe_2O_3 Ratio:	0.18-0.26

Examples of the amounts of raw materials used to make various preferred embodiments of neutral grey glass compositions according to the present invention were set out in Table VI below. The table also details the spectral properties of the resulting glasses:

Table VI

	Example 9	Example 10	Example 11	Example 12	Example 13
Sand	100.00	100.00	100.00	100.00	100.00
Soda Ash	31.41	31.41	31.41	31.41	31.41
Limestone	7.25	7.25	7.25	7.25	7.25
Dolomite	25.83	25.83	25.83	25.83	25.83
Salt Cake	1.0966	1.0959	1.0960	1.0960	1.0961
Sodium Nitrate	0.5198	0.5200	0.5205	0.5207	0.5204
Rouge	2.0996	2.1008	2.1012	2.1010	2.1142
Carbocite	0.0913	0.0910	0.0915	0.0914	0.0913
Cobalt Oxide	0.0300	0.0308	0.0298	0.0305	0.0305
Manganese Dioxide	0.1384	0.2705	0.2800	0.2802	0.5601
Selenium	0.0550	0.0411	0.0418	0.0415	0.0281
Titanium Dioxide	0.0	0.0	0.0	0.0	0.5601
% LTA	18.3	18.8	17.9	19.8	19.5
% UV	7.5	7.4	6.6	8.2	6.0
% IR	15.7	15.6	15.2	15.0	13.1
% TSET	16.7	16.8	16.1	16.9	15.5
Dominant Wavelength	559.8	514.3	463.7	493.9	505.5
Excitation Purity, %	3.3	1.3	5.1	3.8	3.2

As used throughout the disclosure of this invention and in Table VI above, % LTA is defined to be the % luminous

transmittance measured under CIE standard illuminant A. As used herein, the % UV is the % ultra violet transmittance as measured between 280 and 400 nanometres while the % IR is the % infra red transmittance measured over the range of 720 to 2120 nanometres. The % TSET is the % total solar energy transmittance as defined in U. S. Patent # 4,792,536 by the equation:

$$\%TSET = 0.44\ \%LTA + 0.53\ \%IR + 0.03\ \%UV$$

The dominant wavelength and % excitation purity are measured using CIE standard illuminant C.

As discussed herein, glasses containing manganese and iron oxides have been known to solarise or discolour when exposed to a strong ultra violet light source. For example, the Jones patent discussed above teaches that glass containing iron oxide and MnO_2 is undesirable because the MnO_2 causes a brown colouration after UV exposure. In contrast, the glasses of the present invention having the particular set of redox conditions within the scope of this invention, and specifically disclosed in detail above, have been found not to experience any appreciable solarisation. Table VII below shows this. Embodiments of the invention glass according to this invention exhibit only a modest change of the colour after an accelerated 3 month exposure in an Atlas, Model Ci65 Weather-ometer using a Xenon UV lamp. This 3 month exposure in the Atlas Weather-ometer is considered equivalent to over 4 years exposure to the sun in Arizona.

Table VII

	Original	Exposed 3 Months	Difference
Example 14-lab melt-no Mn nor Ti	Dominant Wavelength 483.0	Dominant Wavelength 483.2	+ 0.2
Example 15-lab melt-0.2% TiO_2	Dominant Wavelength 493.2	Dominant Wavelength 494.2	+ 1.0
Example 16-lab melt-0.2% MnO_2	Dominant Wavelength 568.6	Dominant Wavelength 570.2	+ 1.6
Example 17-lab melt-0.4% MnO_2	Dominant Wavelength 557.0	Dominant Wavelength 558.4	+ 1.4
Example 14-lab melt-no Mn nor Ti	% Excitation Purity 5.7	% Excitation Purity 5.4	- 0.3
Example 15-lab melt-0.2% TiO_2	% Excitation Purity 2.9	% Excitation Purity 2.6	- 0.3
Example 16-lab melt-0.2% MnO_2	% Excitation Purity 5.1	% Excitation Purity 5.7	+ 0.6
Example 17-lab melt-0.4% MnO_2	% Excitation Purity 3.9	% Excitation Purity 3.9	0.0

The scope of this invention includes not only glasses with low transmittance but other glasses that have a relatively high LTA which are heat absorbing and have a neutral grey green colour. Exemplary of such glasses are those detailed in examples 18 and 19 in Table VIII below:

Table VIII

	Example 18	Example 19
Sand	100.00	100.00
Soda Ash	31.41	31.41
Limestone	7.25	7.25
Dolomite	25.83	25.83
Salt Cake	1.0960	1.0961
Sodium Nitrate	0.5204	0.5205
Rouge	1.3630	1.3630
Carbocite	0.0912	0.0913
Cobalt Oxide	0.0057	0.0095
Manganese Dioxide	0.2779	0.2779
Selenium	0.0280	0.0210
% LTA	53.2	48.7
% UV	23.9	23.4
% IR	26.4	26.6
% TSET	36.0	34.8
Dominant Wavelength	554.5	512.1
Excitation Purity, %	4.3	1.8

Table VIII above demonstrates glasses made within the scope of this invention which shows the sensitivity of the balance that must be maintained between the cobalt and the selenium. A small increase in cobalt and less selenium moves the dominant wavelength of Example 18 toward a green colour as in Example 19; the excitation purity also is lowered from the cobalt and selenium adjustments made in Example 18 to Example 19.

CLAIMS

1. A heat absorbing, neutral grey coloured glass composition having a base glass composition comprising by weight: 68 to 75% SiO_2, 10 to 18% Na_2O, 5 to 15% CaO, 0 to 10% MgO, 0 to 5% Al_2O_3, and 0 to 5% K_2O, where CaO + MgO is 6 to 15% and Na_2O + K_2O is 10 to 20%, with traces of melting and refining aids, if any, and colourants consisting essentially of: 0.90 to 1.90 wt.% total iron oxide as Fe_2O_3; 0.002 to 0.025 wt.% cobalt as Co; 0.0010 to 0.0060 wt.% selenium as Se; 0.10 to 1.0 wt.% manganese oxide as MnO_2; and 0.0 to 1.0% titanium oxide as TiO_2; the glass at 4 mm. control thickness having light transmittance using illuminant A of 10.0% to 55.0%, ultra violet transmittance less than 25.0%, and infra red transmittance is less than about 50.0%.

2. A neutral grey glass composition according to claim 1, wherein the dominant wavelength is between 470 and 590 nanometres.

3. A neutral grey glass composition according to claim 1, wherein SO_3 is present in the composition in an amount about 0.01 to 0.03 wt. %.

4. A heat absorbing, neutral grey coloured glass composition having a base glass composition comprising: 71 to 74% SiO_2, 13 to 13.80% Na_2O, 8.4 to 8.7% CaO, 3.5 to 4% MgO, 0.15 to 0.25% Al_2O_3, and 0 to 0.1% K_2O, where CaO + MgO is 6 to 15% and Na_2O + K_2O is 10 to 20%, with traces of melting and refining aids, if any, and colourants consisting essentially of: 1.20 to 1.60 wt. % total iron oxide as Fe_2O_3; 0.0160 to 0.0185 wt. % cobalt as Co; 0.0020 to 0.0040 wt % selenium as Se; 0.15 to 0.60 wt. % manganese oxide as MnO_2; and 0.0 to 0.35 wt. % titanium oxide as TiO_2, the glass at 4 mm. control thickness having light

transmittance using illuminant A between 16.0% and 20.0%, ultra violet transmittance between 5 and 10 %, infra red transmittance between 10 and 18 %, and a dominant wavelength between about 470 and 590 nanometres.

5. A neutral grey glass composition according to claim 4, wherein its excitation purity is less than about 5.5%.

6. A neutral grey glass composition according to claim 3, wherein the FeO/total iron oxide as Fe_2O_3 is between 0.18 and 0.26.

7. A neutral grey glass composition according to claim 1, wherein based on 1000 lbs. of sand used in batch ingredients to make said composition, other batch ingredients comprise: 6-24 lbs. salt cake; 3-20 lbs. sodium nitrate; and 0.1-1.5 lbs. carbocite.

8. A neutral grey glass composition according to claim 6, wherein said batch ingredients comprise 8-18 lbs. salt cake; 5-15 lbs. sodium nitrate; and 0.3-1.0 lbs carbocite.

9. A neutral grey glass composition according to claim 8, wherein said batch ingredients comprise 8-12 lbs. salt cake; 5-10 lbs. sodium nitrate; 0.3-1.0 lbs. carbocite; and said neutral grey glass composition comprises 0.15-0.60 MnO_2 and 1.2-1.6 wt. % total iron as Fe_2O_3.

10. A heat absorbing, neutral grey coloured glass composition having a base glass composition comprising by weight: 68 to 75% SiO_2, 10 to 18% Na_2O, 5 to 15% CaO, 0 to 10% MgO, 0 to 5% Al_2O_3, and 0 to 5% K_2O, where CaO + MgO is 6 to 15% and Na_2O + K_2O is 10 to 20%, with traces of melting and refining aids, if any, and colourants consisting essentially of: 0.90 to 1.90 wt.% total iron oxide as Fe_2O_3;

0.002 to 0.025 wt.% cobalt as Co; 0.0010 to 0.0060 wt.% selenium as Se; 0.10 to 1.0 wt.% manganese oxide as MnO_2; and 0.0 to 1.0% titanium oxide as TiO_2; the glass at 4 mm. control thickness having light transmittance using illuminant A of 10.0% to 55.0%, ultra violet transmittance less than 25.0%, and infra red transmittance is less than about 50.0%.T ; and being made from batch materials comprising sand, soda ash, dolomite, limestone, salt cake, rouge, sodium nitrate, a manganese containing compound, carbocite, a cobalt containing compound, and selenium.

11. A neutral grey glass composition according to claim 10, wherein based on 1000 lbs. of said sand in said batch ingredients used to make said composition, said ingredients comprise 6-24 lbs. salt cake; 3-20 lbs. sodium nitrate; and 0.1-1.5 lbs carbocite.

12. A neutral grey glass composition according to claim 11, wherein said ingredients comprise 8-18 lbs. salt cake; 5-15 lbs. sodium nitrate; and 0.3-1.0 lbs. carbocite.

13. A neutral grey glass composition according to claim 12, wherein said ingredients comprise 8-12 lbs. salt cake; 5-10 lbs. sodium nitrate; 0.3-1.0 lbs. carbocite; and said neutral grey glass composition comprises 0.15-0.60 MnO_2 and 1.2-1.6 wt. % total iron as Fe_2O_3.

14. A glazing for automotive or architectural use prepared from the neutral grey glass composition of claim 1.

15. A process for preparing a neutral grey glass composition having at 4 mm. control thickness a light transmittance using illuminant A of 10.0% to 55.0%, ultra violet transmittance less than 25.0%, and infra red transmittance is less than about 50.0%., consisting essentially of admixing and melting together sand, soda ash, dolomite, limestone, salt cake, rouge, sodium nitrate, a

manganese containing compound, carbocite, a cobalt containing compound, and selenium, in quantities sufficient to form the glass of composition as claimed in any one of claims 1 to 13.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/02496

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C4/02 C03C3/087

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 162 835 (GLAVERBEL) 12 February 1986 see page 2, line 19 - line 40 see claims; examples I,J,N,P ---	1-6,10, 14,15
A	CHEMICAL ABSTRACTS, vol. 106, no. 12, 23 March 1987, Columbus, Ohio, US; abstract no. 89151c, G.I.ARTAMONOVA ET AL. 'glass' page 289 ; see abstract & SU,A,1 270 133 (STATE SCIENTIFIC-RESEARCH INSTITUTE OF GLASS) 15 November 1986 ---	1,4

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
15 February 1995	22.02.95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Puetz, C

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 7721, Derwent Publications Ltd., London, GB; AN 77-37284Y & JP,A,52 047 811 (SHIN NIPPON GLASS) 16 April 1977 see abstract	1,4
A	EP,A,0 349 909 (PPG INDUSTRIES) 10 January 1990 cited in the application see the whole document	1-6,10, 14,15
A	US,A,5 023 210 (KRUMWIEDE ET AL.) 11 June 1991 cited in the application see the whole document	1-6,10, 14,15
A	EP,A,0 482 535 (PPG INDUSTRIES) 29 April 1992 see page 2, line 1 - line 7 see page 3, line 13 - line 43 see claims 1-7	1-6,10, 14,15
A	EP,A,0 536 049 (SAINT-GOBIN VITRAGE INTERNATIONAL) 7 April 1993 see claims 1,2,4,5,9,10,12; examples 1,13	1-6,14, 15

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